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14. ABSTRACT A diallyl-terminated spiro orthocarbonate was synthesized via a multi-step procedure. Polymer blends of SOC/bismaleimide were formed. DSC and FTIR confirmed that cationic-catalyzed ring opening was achieved. Volume expansion was measured and found to be related to the concentration of SOC in the formulation. The underlying mechanism for such expansion was analytically modeled using quantum chemical calculations that correlates with experimental results. Adhesive preregs of the SOC-bismaleimide polymer blends were prepared and good quality lap-shear specimens were fabricated. Data indicate that the blends were at least as good as the baselines.					
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Executive Summary

This report describes the result gathered in a 12-month STTR program to develop high temperature low cure shrinkage adhesives. Adhesively bonded structures offer weight savings, ease of fabrication, and absence of stress concentrations arising from holes and fasteners. However, the reduction in volume often creates internal strain in the resin, and often lead to loss of adhesion at the interface. This program describes a methodology that seeks to reduce the extent of volume reduction by the use of polymer blends containing monomers that expand via ring opening during cure, thus compensating for the loss in volume.

The literature reveals that a variety of bicyclic monomers would undergo double ring opening with either no change in volume or actual expansion. Among these classes of heterospirocyclic monomers, spiro orthocarbonate (SOC) derivatives have shown significant potential as monomers which show no shrinkage on polymerization. However the use of these monomers in high temperature polymers and adhesives has not been reported. We therefore extended this knowledge and used SOC as comonomers in the cure of high temperature polymers so as to demonstrate its effectiveness in reducing the shrinkage of high performance adhesives.

A diallyl-terminated spiro orthocarbonate was synthesized via a multi-step procedure. By blending the diallyl SOC with bismaleimides, the SOC was inserted into the microstructure of the polymer network. Subsequently when the bicyclic ring structure was cleaved open, volume expansion can potentially reduce volume shrinkage of the bismaleimide network. Various formulations of polymer blends containing different ratios these expandable monomers were synthesized. Differential scanning calorimetry and infrared spectroscopy confirmed that cationic-catalyzed ring opening could be achieved within the cure cycle for the bismaleimide resin. Volume expansion was measured and was found to be related to the concentration of the SOC in the formulation. The underlying mechanism for such expansion was analytically modeled using quantum chemical calculations, from which the theoretical volume expansion was found to be reasonably close to that obtained empirically. Prepregs containing the SOC-blended bismaleimides were easily fabricated, and good quality lap-shear specimens were also easily fabricated under conventional processing condition. Preliminary data indicated that the SOC-blend yields were comparable to those of the baseline bismaleimides. Detail mechanical data were not obtained due to time/material constraints, however.

The work in Phase I have demonstrated the feasibility of using of expanding monomers as comonomers in polymer blends to reduce cure shrinkage in high performance adhesives. Further development in Phase II will lead to the technology demonstration of this concept, leading to the field demonstration and pilot production of the adhesives.

1. Introduction

The formation of polymers from smaller monomers is usually accompanied by a reduction in the volume of the final polymer network. This shrinkage creates internal strain in the resin, may cause it to pull away from the reinforcing fibers, fillers or adherends, resulting in loss of adhesion, potentially creates voids or channels for the penetration of moisture and other degradation agents. The internal strain also diminishes the mechanical properties of the resins, adversely affecting the performance and durability of the bonded structures. Therefore polymer systems that can cure with reduced or no shrinkage can be expected to have enhanced mechanical properties and longer service lives.

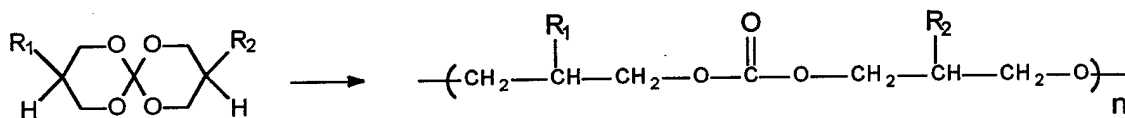
Other technology areas that are in critical need of polymers and adhesives with reduced shrinkage are in the fabrication and packaging of microelectronic and electro-optical devices. For example, polymer cure shrinkage affects the linearity and pitch (spacing) of the conductors placed on polymeric dielectric films; adhesive shrinkage may exceed the fracture toughness of silicon dies, leading to die-cracks which destroys the device; adhesive shrinkage may also cause misalignment of optoelectronic elements.

2. Technical approach

Strategies to minimize polymerization shrinkage include maximization of the filler concentration, formulating resin phases based on low shrinking oligomers, synthesis of monomers that expand on polymerization, and designing composites that undergo post-cure expansion due to water uptake, and modifying processing cycles.¹ A search of the literature shows that polymerization shrinkage has been recognized to be caused by two factors:

- (a) The replacement of van der Waals interactions among the monomers by the shorter (by about one third) covalent bonds of oligomers and polymers;
- (b) An increase in packing density of polymer chains upon cure when compared with the packing of monomer molecules (disregarding crystallization).

In the effort to address factor (a), it has been demonstrated that a variety of bicyclic monomers would undergo double ring opening with either no change in volume or actual expansion², as shown below:



The list includes spiro orthoesters (SOE), spiro orthocarbonates (SOC), bicyclic orthoesters (BOE), bicyclo ketal lactones, trioxabicyclooctanes and unsaturated diketals of benzoquinone. Bailey *et al.*³ reported that the volume expansion upon homopolymerization of the monomers themselves can range from 5-15%. He *et al.*⁴ found that dependent on the exact ratios of the reactants, epoxy/spiro orthocarbonates can be formulated to provide a net zero expansion, so that the adhesive joint is essentially stress-free. Recently it was found that some of these monomers could be used as diluent comonomers for dental resins to reduce polymerization shrinkage.^{5,6} Among these classes of heterospirocyclic monomers, SOC derivatives have shown significant potential as monomers which show no shrinkage on polymerization. We therefore intend to take advantage of this knowledge and propose to use SOC as comonomers in the cure of high temperature polymers so as to demonstrate its effectiveness in reducing the shrinkage of high performance adhesives.

The hypothesis that minimizing factor (b) can lead to lowered cure shrinkage was first predicted by Tager *et al.*⁷ who calculated that among polyacrylate and polymethacrylates, contraction due to denser packing of chains should decrease for highly branched monomers due to increased steric hindrance. Later Holter *et al.*⁸ confirmed that by increasing the volume of the attached side groups in branched bis-methacrylates (e.g. bisphenol A glycidyl methacrylate), total volume shrinkage decreases with growing lengths of the alkyl chains. Similarly Miyazaki⁹ showed that by attaching SOC as pendant group in methacrylates, the SOC upon ring opening expands into highly branched pendant groups and reduces the overall polymerization shrinkage. We therefore

intend to demonstrate the potential of SOC-pendent monomers to decrease cure shrinkage.

Nevertheless, although the synthesis, polymerization and potential of these expanding monomers are well established, their use as comonomers or polymer blends to reduce cure shrinkage in high performance adhesives, such as imides or bismaleimides, have not been reported. By building upon prior published work, we have an opportunity to proceed with this project expeditiously. We are confident that at the conclusion of this Phase I, the feasibility of this concept would be demonstrated satisfactorily.

3. Experimental

3.1 Synthesis of tetraethyl orthocarbonate (1)

A solution of sodium ethoxide was prepared under nitrogen from 70 g (3.04 g. atoms) of sodium and 2 L of absolute ethanol in a 3-L three-neck flask that was equipped with a mechanical stirrer, a condenser and dropping funnel. Chloropicrin (100 g, 0.61 mole) was placed in the dropping funnel, and the stirred solution was heated to 58-60°C with a water bath. The chloropicrin was added dropwise at a rate so that the exothermic reaction was maintained at 58-60°C when the water bath was removed. The solution was allowed to stand overnight. About 60% of the ethanol was removed by distillation under reduced pressure, using a 45-50°C water bath as the heat source. The residue was cooled, diluted with 1 L of water and transferred to a separatory funnel. The organic layer was separated, washed with water and dried over anhydrous magnesium sulfate. The aqueous layer was extracted with several portions of ether, the extracts were combined, washed with water, dried over magnesium sulfate, and combined with the organic portion. The combined crude product was fractionally distilled at atmospheric pressure to obtain tetraethyl orthocarbonate at 40% yield, b.p. 158-161°C, as reported in the literature.

3.2 Synthesis of 2-allyl-1,3-propanediol (2)

To a suspension of LiAlH_4 (11.89 g, 313.3 mmol) in absolute ether (300 mL), a solution of diethyl allylmalonate (24.88 g, 124.3 mmol) in absolute ether (10 mL) was added dropwise at room temperature. After the addition, the mixture was refluxed for 1 h and stirred overnight at room temperature. Water was slowly added to destroy the hydride. A white mass was filtered and the filtrate was evaporated. And the residue was fractionally distilled to obtain 2-allyl-1,3-propanediol (11.5 g, 80% yield, bp 0-93°C/1 torr).

3.3 Synthesis of diallyl spiro orthocarbonate (3)

Diol **2** (13.68 g, 117.8 mmol) and tetraethyl orthocarbonate **1** (11.33 g, 58.9 mmol) were heated at 110°C for 9 h in the presence of anhydrous *p*-toluenesulfonic acid (0.12 g), and the ethanol was collected in a trap. Triethylamine (0.24 mL) was added, and the solution was allowed to stand at room temperature overnight. The mixture was fractionally distilled to obtain diallyl spiro orthocarbonate **3** (13.45 g, 95% yield, bp 128-131°C/0.1 torr).

3.4 Polymerization of Bismaleimides and Blends

Matrimid 5292™. The material was obtained from Ciba Geigy as two components, 5292A and 5292B. Equimolar amounts of the components were dissolved in tetrahydrofuran, heated to complete dissolution, evaporated, and vacuum dried at room temperature.

Bismaleimide/spiro orthocarbonate Blends. Similarly, the required amounts of Matrimid and spiro orthocarbonate **3** were co-dissolved in tetrahydrofuran, evaporated and vacuum dried.

3.5 Specific Gravity Measurements of Polymer Blends

For blends that contain spiro orthocarbonate, the uncured mixture is a viscous paste at room temperature. The uncured blend was warmed to induce flow and charged into the pycnometer, and specific gravity measurements were obtained according to ASTM D369-84. Once partial cure was achieved, specimens could be obtained conveniently from aluminum molds that were heated at predetermined intervals and specific gravity measurements were obtained according to ASTM D792-91.

3.6 Adhesive Prepregging

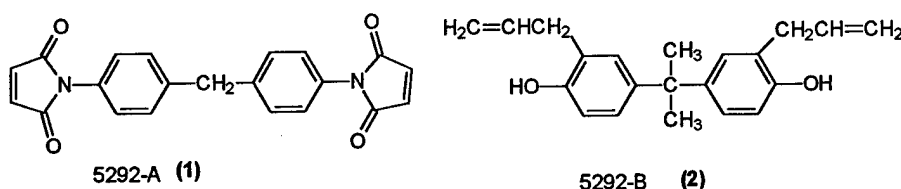
The amount of monomers needed to yield a prepreg with 60% resin content was dissolved in warm tetrahydrofuran and transferred to a Teflon-lined pan containing a E130 glass fabric. The solution was allowed to evaporate and vacuum dried.

3.7 Adhesive Joints Fabrication

Eight-ply graphite fiber reinforced PMR-15 laminates were cut into 6" x 4" plaques. The plaques were cleaned with MEK. 1-inch widths of the plaques (along the long dimension) were sanded with sandpaper, rinsed well with MEK and the plaques were vacuum dried. Lap shear joints were fabricated with 0.5-inch joint widths and cured at 0.1 Mpa (15 psi) pressure. Cure cycle is 3 hr at 150C, 3h at 200C, and postcured 6h at 250C. One-inch wide lap-shear specimens were cut from the plaques. Lap shear strengths were measured at room temperature at 1.27 mm/min (0.05 in/min).

4. Results and Discussion

When a state-of-the-art bismaleimide such as Ciba-Geigy 5292® cures, the maleimide (5292-A) reacts via free radicals with the diallyl groups of its comonomer, diallyl bisphenol A (5292-B), with the potential for volume shrinkage. Two types of unsaturated SOC's are to be prepared to use as blends to mitigate cure shrinkage, as discussed below.



The purpose of this program is to demonstrate that a diallyl-terminated spiro orthocarbonate, 3,9-diallyl-1,5,7,11-tetraoxaspiro[5.5]undecane (3) can completely or partially replace 5292-B, which can later undergo expansion via cationic ring-opening of the highly strained central spiro moiety, as shown in Figure 3. This "unpacking" creates volume expansion, which can be tailored by the concentration of the diallyl SOC in the formulation.

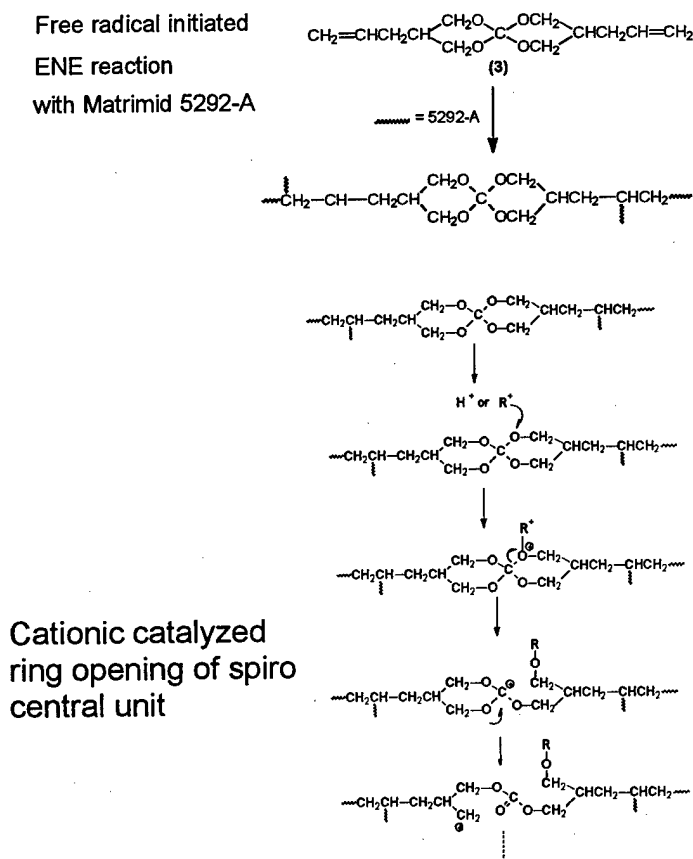


Figure 3. Ring opening of bismaleimide/spiro orthocarbonate for volume expansion

4.1 Fourier Transform Infrared Spectroscopy

The cure of the diallyl SOC/bismaleimide blend was monitored by FTIR. Ordinarily the appearance of the carbonyl stretching band at $1700\text{--}1750\text{ cm}^{-1}$ is the best indication of ring opening of the spiro orthocarbonate groups. However, the existence of the four carbonyl groups per bismaleimide on Matrimid 5292A® made this peak assignment impossible. Therefore the appearance of ester absorption bands were used instead. As shown in Figure 4, the diallyl SOC/BMI blend after cure show the appearance of absorption bands at 1776 cm^{-1} and 1172 cm^{-1} , which we assign to the carboxylic ester C-O stretching. In addition, the carbonyl absorption peak at 1710 cm^{-1} is broader and stronger in the cured sample, indicating the increased concentration of C=O groups. Similarly, the C-O stretching at 1172 cm^{-1} in the cured sample is much broader and stronger than the C-O absorption in the monomer (1148 cm^{-1}), probably due to the opening of the highly strained spiro configuration.

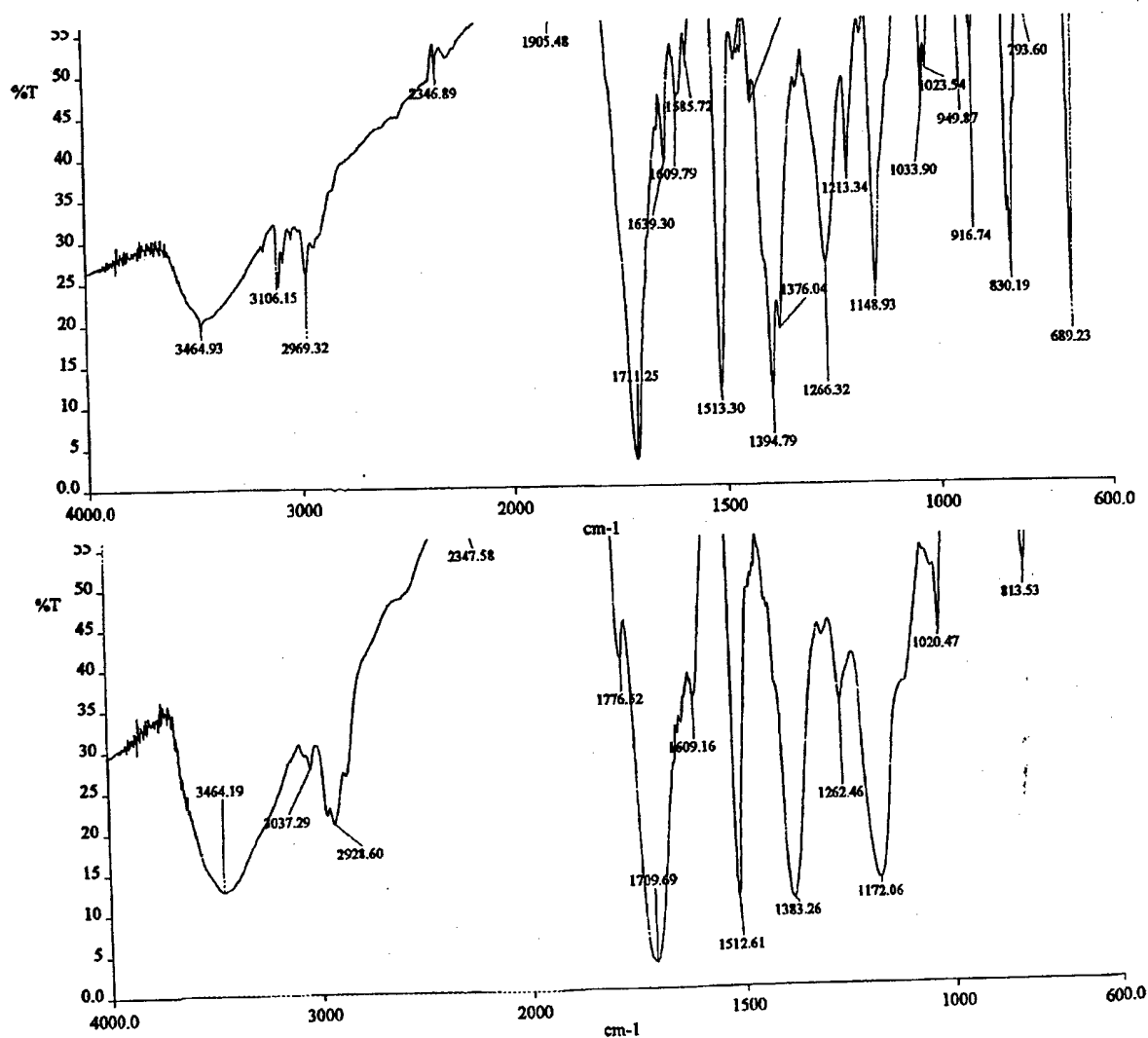


Figure 4. FTIR spectra of diallyl SOC/Matrimid 5292A blends. Upper: Monomer blend; Below: cured for 2h at 150°C 2 h at 200°C, postcured 6h at 150°C

4.2 Differential Scanning Calorimetry.

In order to identify the reactivities of the diallyl SOC/BMI blends, DSC of some representative blends were obtained, as shown in Figure 5. The formulations of these blends are as follows, in mole %:

	5292-A	5292-B	Diallyl SOC	Cationic Initiator	Free radical Initiator
F (baseline)	1.0	1.0			
C	0.5		0.5	0.005	
G	0.5	0.25	0.25	0.005	0.005

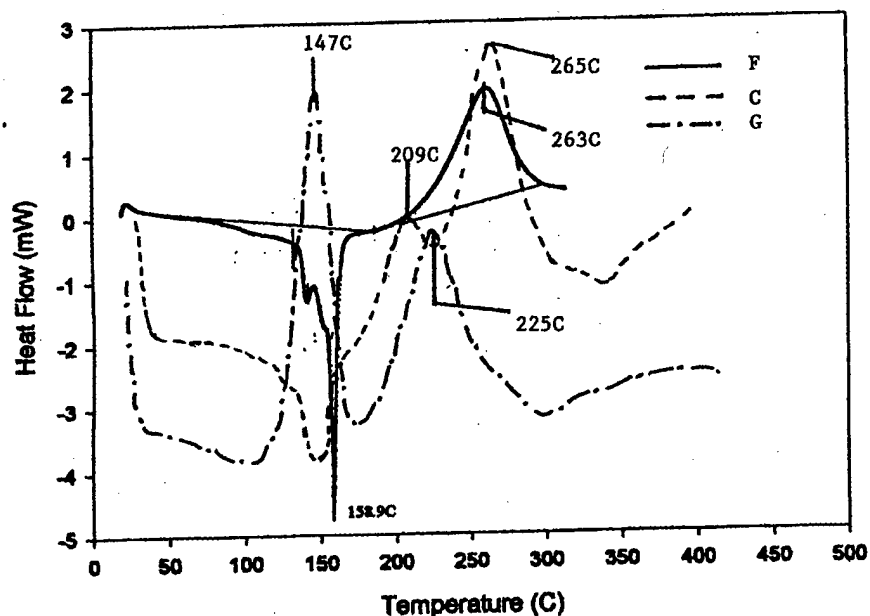


Figure 5. Polymerization DSC of diallyl SOC/BMI Blends (see text for sample formulations)

During cure Matrimid 5292® goes through a melting transition at 158°C and a broad exotherm peaking at 263°C as it goes through polymerization and crosslinking "ENE" reaction. Because ring opening of the spiro functionality is a cationic reaction, we prepared Sample C, in which 5292-B was replaced by diallyl SOC, and a cationic initiator (triphenyl sulfonium hexafluoroantimonate) was added. The sample shows that in addition to a similar polymerization and crosslinking exotherm at 265°C, there appeared an exotherm at 209°C, which must then be the ring opening of the central spiro unit. However, to achieve the most effective shrinkage mitigation, it is preferable that the polymer chain propagation be substantially accomplished prior to the unpacking of the central spiro entities. By adding a free radical initiator (*tert*-butyl peroxybenzoate), which has a decomposition temperature of about 110°C, Sample G shows an exotherm at 147°C, which is probably the free radical initiated polymerization, followed by a cure

peak of 225°C. The previous exotherm at 265°C but have shifted to a lower temperature (225°C), seemingly merging with the ring opening reaction.

4.3 Quantum Chemical End-To-End Distance Computation for Cure Volume Change Prediction

In order to analytically describe volume changes during cure, ring opening or steric hindrance effects have to be taken into account. One way to account for this type of curing structural changes is the use of quantum chemical computation such as Gaussian 94¹⁰. Gaussian 94 optimizes the conformation of a polymer structural unit by its energy to the most stable spatial arrangement. Having obtained this stable conformation, the end-to-end distance can then be employed to infer its spatial volume. In general the end-to-end distance between atom *i* and atom *j* is denoted as d_{ij} . In this case, the calculated d_{C1-C23} based on quantum chemistry is 5.78 Å (see Figure 6 and Table V). For the SOC ring opened structure (Fig. 6), these same two carbon atoms, C1 and C21 (note that the initial C23 is now assigned a different atom number C21 for ease of quantum mechanics computations), have taken on an increased end-to-end distance of 6.89 Å, clearly inferring the potential for volume expansion. Similarly, d_{C1-C15} in the initial SOC structure has increased from 3.77 Å to 7.66 Å (d_{C1-C29}) due to ring opening during cure, again showing the possibility of a large volume expansion. This inferred volume expansion produced by ring opening can also be seen from the change of interatomic distance, $d_{C14-C15}$, of 1.3962 Å to that of $d_{C13-C29}$ at 4.6766 Å in the ring opened structure. Table V lists these end-to-end distance increases, strongly suggesting a volume expansion from ring opening of SOC during cure. Furthermore, the calculated heats of formation for the initial SOC and the ring opened structures are -167 and -284 Kcal/mole, respectively, meaning that the latter is the energetically preferred conformation due to its much lower heat of formation.

During the cure of SOC and Matrimide 5292A, the double bonds open to form single bonds. Indeed, as shown in Table V, the calculated d_{C1-C29} and d_{C1-C31} (see Fig. 6) are seen to be 3.61 and 3.47 Å, respectively, showing the expected decrease of end-to-end distance from the conversion of a double bond to a single bond due to cure. Thus, the quantum chemistry end-to-end distance computations infer the effects of conformational constraint and ring opening to predict cure shrinkage and/or cure expansion.

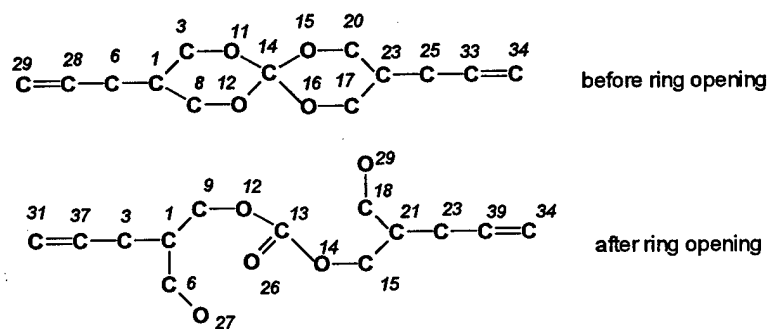


Figure 6. Nomenclature for quantum mechanical calculations (see text for analysis)

Table VI. Theoretical Volume Changes During Cure

	Volume Change, %
Matrimid 5292-A + 5292-B (1:1)	+5.13
Matrimid 5292-A + diallyl SOC (1:1)	-1.82

The calculations show that based on theoretical calculations, there is a volume expansion when diallyl SOC is incorporated into a polymer matrix.

4.4 Experimental Measurement of Volume Expansion During Cure.

By adjusting the concentration of diallyl SOC in the formulations, various degrees of volume expansion were obtained, as shown in Table VII. The specific gravity of the monomeric blends were measured by pycnometry (ASTM D369-84) and the cured samples by displacement (ASTM D792-91).

Table VII. Cure Shrinkage Measurements of Polymer Blends Containing Diallyl Spiro Orthocarbonate

Sample	Specific Gravity (t=0)	Specific Gravity (3h@150C)	Specific Gravity (3h@150C+3h@20 0C+6h@250C)	Total volume change, %
C	1.2402	1.2391	1.0724	+13.5
D	1.1967	1.126	1.0986	+8.2
F (Matrimid®)	1.2162	1.2404	1.2794	-5.2
Formulations	5292-A (mole %)	5292-B (mole %)	Diallyl SOC (3) (mole %)	Cationic catalyst (mole %)
C	0.5	0	0.5	.005
D	0.5	0.25	0.25	.005
F (Matrimid®)	0.5	0.5		

The data in Table VII show that spiro orthocarbonate compounds can effectively counteract volume shrinkage during cure. We therefore propose to further develop this approach in Phase II, using diallyl spiro orthocarbonate (3) as one of the candidates.

4.5 Thermogravimetric Analysis

The thermal stability of SOC-containing blends was compared with the baseline bismaleimide resins by thermogravimetric analysis. Figure 6 shows that the addition of spiro orthocarbonate in the polymer network did not appreciably alter the resin's thermal stability when compared with the unmodified BMI resin.

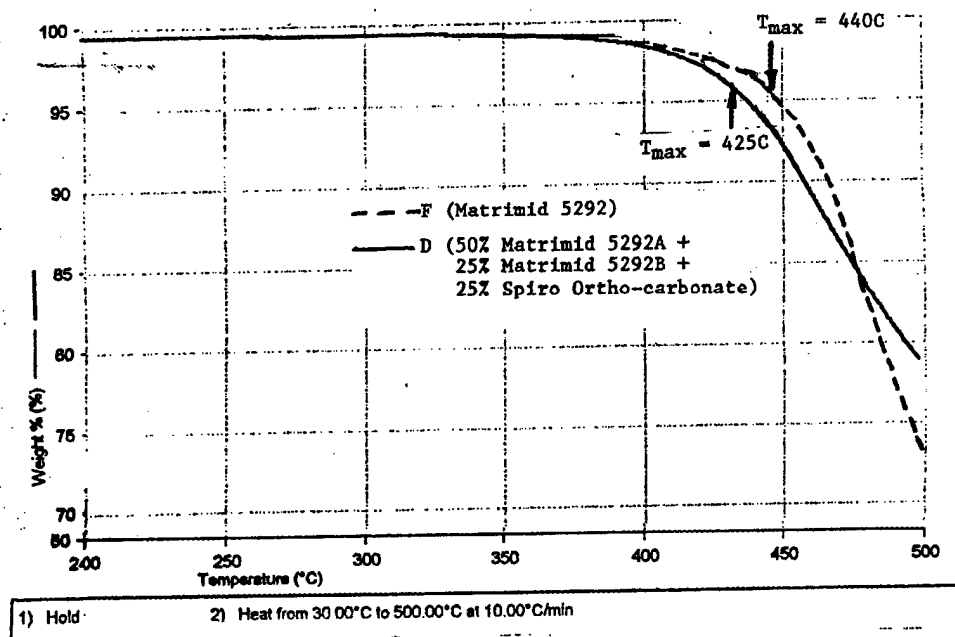


Figure 6. Thermogravimetric analysis of bismaleimide resins with and without spiro orthocarbonate

4.6 Adhesive Prepregging and Joint Fabrication

Adhesive prepregs were prepared by solution impregnation using E120 glass fabric as the carrier and contains 60% resin content. Lap shear specimens were prepared using carbon reinforced PMR15 composites as substrates. The composite panels, measuring 4" x 6" were solvent wiped and cleaned with 120 and 220 sandpapers. Lap joints with 0.5 inch overlap were fabricated and cured in a heated press at 50psi. The cure cycle was 3 hours at 150C, 3 hours at 200C and postcured for 6 hours at 250C. One inch wide lap shear joint specimens were cut from the cured panels. Lap shear strengths were measured at room temperature at a crosshead speed of 0.05 inch/min. The data are as follows:

Baseline Matrimid (in psi): 905, 953, 880, Ave = 912 psi
 Formulation D (in psi): 950, 910, 902, Ave = 920 psi

Thus the SOC blended formulation was shown to be at least comparable to that of the baseline bismaleimide. However, the specimens all showed areas of adhesive failure, indicating improved surface preparation work is needed, perhaps in form of priming the surfaces, before the advantages of SOC-blended formulation can be quantified.

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